

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 989 105 A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(43) Date of publication:

29.03.2000 Bulletin 2000/13

(51) Int. Cl.⁷: **C07B 63/00**

(21) Application number: 99913604.7

(86) International application number:

PCT/JP99/01896

(22) Date of filing: 09.04.1999

(87) International publication number:

WO 99/52841 (21.10.1999 Gazette 1999/42)

(84) Designated Contracting States:

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE

• FUJII, Takahisa

Nagaokakyo-shi, Kyoto 617-0836 (JP)

• MIKI, Wataru

Hyogo-ku, Kobe-shi, Hyogo 652-0803 (JP)

• NAGAMI, Kenzo

Osaka-shi, Osaka 532-0005 (JP)

• ARAI, Kunio

Sendai-shi, Miyagi 982-0032 (JP)

(30) Priority: 09.04.1998 JP 9781998

(71) Applicant: SUNTORY LIMITED

Osaka-shi, Osaka 530-8203 (JP)

(74) Representative: HOFFMANN - EITLE

Patent- und Rechtsanwälte

Arabellastrasse 4

81925 München (DE)

(72) Inventors:

• NAKAHARA, Koichi

Toyonaka-shi, Osaka 560-0861 (JP)

**(54) PROCESS FOR PRODUCING AROMATIC COMPOUNDS VIA TREATMENT WITH
SUPERCRITICAL WATER**

(57) The present invention provides a process for producing aromatic compounds or polymers thereof from a plant material in a short period of time and by a simple procedure. Concretely, the process treats the plant material with supercritical water or subcritical water to liberate aromatic compounds, which are contained in the plant material, and/or aromatic compounds, which have been generated upon decomposition of components of the plant material, to the outside of the plant material, and isolates the liberated aromatic compounds to produce aromatic compounds or polymers thereof.

EP 0 989 105 A1

Description

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to a process for producing aromatic compounds from a plant material. More particularly, the invention relates to a process for producing aromatic compounds in a short period of time and by a simple procedure involving treatment of a plant material with water which is in a supercritical state or subcritical state.

Prior Art

[0002] Plant materials are known to contain polymeric compounds, such as lignin and ellagitannin, having various aromatic compounds, such as vanillin, gallic acid, ellagic acid, and protocatechuic acid, as constituent units. Hitherto known methods for obtaining aromatic compounds contained in plant materials have been only extraction methods involving radical decomposition, such as thermal modification (Japanese Patent Public Disclosure (Kokai) No. 59519/97), electron beam irradiation (Japanese Patent Public Disclosure (Kokai) No. 121392/75), and explosive disintegration (Japanese Patent Public Disclosure (Kokai) Nos. 19895/86, 222802/88, 117400/90, 126725/92, and 145027/92).

[0003] Many aromatic compounds have characteristic aromas. Vanillin is an aromatic compound used widely as an edible perfume in foods such as ice cream and candies, and as a flavor in luxury products such as liqueur and tobacco. Industrially, vanillin is synthesized by methylating protocatechualdehyde, which is derived from eugenol or safural, with an alkali and dimethyl sulfate, or by oxidatively treating lignin sulfonic acid contained in sulfite pulp waste liquor. A method of extraction from vanilla beans is also performed, but can obtain only a trace amount of vanillin from a large amount of a raw material. Syringaldehyde, an aromatic compound, is known as an aroma component of sake, but a method for commercial production of this compound has not been known. Gallic acid is utilized as a deoxidizing agent, a developer for photography, a starting material for inks and dyes, an astringent, or a hemostatic.

[0004] Various application studies are under way with regard to extraction, purification, synthesis and decomposition using supercritical fluids. For supercritical water, studies on its capacity to detoxify PCB and dioxin (Japanese Patent Public Disclosure (Kokai) No. 327678/97) are being carried out, and its degradation reaction of biomass is also being investigated. Japanese Patent Public Disclosure (Kokai) No. 31000/93 reports a method which selectively hydrolyzes or pyrolyzes natural or synthetic high molecular compounds with the use of supercritical water as a solvent to decompose the polymers into their constituent units or into approximately oligomeric combinations of the constituent units. Examples of this method include forma-

tion of glucose from cellulose contained in large amounts in polymeric resources, such as paper, wood and straw, and conversion of lignin-derived specimens into low molecular compounds. Japanese Patent Public Disclosure (Kokai) No. 268166/97 describes a method for producing various amino acids by hydrolyzing proteins with water present in a supercritical state.

[0005] However, it has not been known that it is possible to obtain aromatic compounds by treating plant materials with water present in a supercritical state.

SUMMARY OF THE INVENTION

[0006] The present invention provides a process for producing aromatic compounds from a plant material in a short period of time and by a simple procedure.

[0007] The present invention further provides a process for producing aromatic compounds, which process does not discharge waste generated as squeeze leavings as results from conventional methods such as thermal modification.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

FIG. 1 is a view showing the results of high performance liquid chromatography of aromatic compounds obtained from a *Quercus crispula* material. FIG. 2 is a view showing the results of high performance liquid chromatography of aromatic compounds obtained from a Japanese cedar material. FIG. 3 is a view showing the results of high performance liquid chromatography of aromatic compounds obtained from a hinoki material. FIG. 4 is a view showing the results of high performance liquid chromatography of aromatic compounds obtained from a bamboo material.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention is a process for producing aromatic compounds derived from a plant, or polymers of the aromatic compounds, in a short period of time and by a simple procedure, the process comprising treating a plant material with supercritical water or subcritical water to liberate aromatic compounds, which are contained in the plant material, and/or aromatic compounds, which have been generated upon decomposition of components of the plant material, as individual compounds or polymers thereof to the outside of the plant material; and separating and purifying the liberated aromatic compounds or their polymers.

Aromatic compounds

[0010] The aromatic compounds and their polymers, obtained by the process of the present invention, range

variously according to the type of the plant material used. Typical aromatic compounds or polymers thereof include the following:

a) Phenylpropanoids

Vanillin, vanillic acid, coniferyl aldehyde, coniferyl alcohol, syringe, syringic aldehyde, syringic acid, sinapic acid, and polymers of these.

b) Pyrogallol derivatives

Pyrogallol, gallic acid, ellagic acid, and polymers of these.

c) Pyrocatechol derivatives

Pyrocatechol, protocatechuic acid, and polymers of these.

Plant materials used

[0011] The kinds of plants used as starting materials are not restricted, but examples include bamboo, Japanese cedar, hinoki, *Quercus crispula*, cherry tree, Japanese horse chestnut, pine tree, hiba arborvitae, Japanese chestnut tree, bamboo grass, oak, paulownia, Japanese apricot, peach, maple tree, zelkova tree, wisteria, fir, elm, ginkgo, camellia, willow, mulberry, teak, mahogany, magnolia, persimmon, apricot, Chinese quince, sweet brier, rose, loquat, Japanese quince, fragrant olive, camphor tree, Japanese yew, acacia, and prickly shrub of *Araliaceae*.

[0012] In the present invention, any parts of these plants can be used, such as trunk, bark, stalk, branch, root, leaf, flower, bud, and seed. Typically, a woody portion or a floral portion is used. For example, it is preferred to use wooden-type containers which were used for the production and/or storage of fermented products and foods and drinks as plant materials in order to effect utilization of waste materials. Preferably, a plant material is subjected to fine chopping, thin cutting, or powdering as pretreatment to make supercritical water treatment efficient and increase the recovery of aromatic compounds or their polymers.

Conditions for supercritical water treatment

[0013] The process of the present invention is characterized by treating a plant material with supercritical water.

[0014] It is well known that substances can exist in three states: as a solid, liquid or gas. If temperature and pressure are gradually increased, starting in a state in which a gas and a liquid mingle, when a certain pressure and a certain temperature (i.e., critical point) are exceeded, there exists a range in which the boundary surface between the gas and the liquid disappears, and the gas and liquid integrate as an inseparable entity to form a fluid state. Such a fluid is called a supercritical fluid, which is a high-density fluid having properties intermediate between gas and liquid. That is, this fluid, like a liquid, dissolves various substances, and has high

fluidity like a gas.

[0015] The critical point for water is a temperature of 374°C and a pressure of 221 atmospheres. Supercritical water refers to water in a state at a temperature and a pressure in specific ranges exceeding this critical point. Supercritical water continuously varies in the values of parameters, such as density, viscosity, dielectric constant, ion product, and diffusion coefficient, depending on temperature and pressure. Solubility, an important parameter for a reaction solvent, is known to increase as density increases. Another factor related to solubility is dielectric constant, which increases with increasing density, and decreases as temperature rises. At a sufficiently high temperature, a dielectric constant becomes so small that water is almost unable to shield the electrostatic force working among ions. Under these conditions, most of the dissolved ion species are present as ion pairs. Thus, supercritical water behaves as a nonpolar substance, rather than as a polar substance. Incidentally, the pH of water in a supercritical state is 4, producing a hydrogen ion concentration of 1/10,000, while the hydroxide ion concentration is also 1/10,000. Hence, it will be readily apparent that the properties of this water are entirely different from those of water as a liquid.

[0016] The present invention produces aromatic compounds by utilizing the foregoing features of supercritical water. Therefore, compared with the conventional technology for producing aromatic compounds from a plant material by thermal modification (Japanese Patent Public Disclosure (Kokai) No. 59519/97), the present invention does not generate by-products which otherwise appear secondarily as a result of a heating method. In this respect, this invention is essentially different from the conventional technology, and can produce aromatic compounds in high yields with ease and in a short time. In light of this feature of the present invention, it can be easily predicted that treatment of a plant material with subcritical water next to supercritical water would similarly be able to obtain aromatic compounds. Hence, references, to be made hereinbelow, to supercritical water also include subcritical water, as will be clear from the context.

[0017] During supercritical water treatment, the plant material and water are mixed, for example, at a plant material-to-water ratio of 1:about 1 to 1,000, preferably, 1:about 5 to 200. The reactor may be any container suitable for supercritical water treatment, and may be selected, as desired, according to the scale of production. For example, a closed container (preferably one made of a metal such as SUS alloy) with a capacity of about 1 ml to 10 liters, preferably about 10 ml to 1 liter, is used. This container is charged with about 30 to 40% (V/V), preferably 32 to 35% (V/V), of water, and the plant material is added at the above-mentioned ratio. To produce aromatic compounds, treatment is preferably performed in an anaerobic state. For this purpose, it is advisable to evacuate the inside of the container, or fully

purge the inside of the container and water with an inert gas such as nitrogen or argon, followed by closing the container. Treatment is performed under conditions under which water is in a supercritical state at a temperature of about 374°C (pressure at this time is about 221 atmospheres or more) to about 500°C (about 300 atmospheres or more), or under conditions under which water is in a subcritical state at a temperature exceeding about 300°C (exceeding about 150 to 200 atmospheres). The treatment time is within about 30 minutes, preferably within about 2 minutes.

[0018] The conditions for the treatment time and temperature are selected from the above-described ranges, according to the plant material used as the starting material, the aromatic compounds intended for production, or various conditions, such as the scale of production. For example, polymers of various aromatic compounds can be obtained by setting a shortened reaction time or a lowered reaction temperature. Concrete conditions for such purposes can be determined easily by experiments.

Separation and purification of aromatic compounds

[0019] The plant material treated with water in a supercritical state is cooled by a means such as rapid cooling of the reactor containing the material with iced water or the like. After making sure that the temperature has been sufficiently lowered, the reactor is opened. Normally, water soluble substances are recovered as an aqueous solution, while liposoluble substances adhere to the wall surface of the reactor in a tarry form. Aromatic compounds often show fat solubility, so that the portion adhering to the wall surface is recovered with the use of an organic solvent, such as alcohols, acetone, dimethyl sulfoxide, or acetonitrile. The recovered liposoluble mixture is pretreated, as required, with activated charcoal or an adsorbent carrier. Then, the mixture is used, as such or after separation and purification into respective compound groups or individual compounds in certain cases, according to the purpose of use. Purification methods rely on, but are not restricted to, various chromatographic techniques using silica gel, octadecyl-, cyanopropyl-, or t-butyl-modified silica gel, a cation or anion exchanger, hydrophobic resin, or cellulose as a carrier, electrophoresis, use of various separation membranes, use of various resins, and liquid-liquid distribution.

[0020] The tarry substance after extraction of the aromatic compounds is likely to contain other useful components. For example, essential oil components can be isolated by further extraction with hexane-diethyl ether.

[0021] The aqueous solution recovered from inside the reactor may contain low molecular compounds such as glucose or lignin. These compounds may be isolated separately, if desired.

Example 1

[0022] A *Quercus crispula* material was cut thinly with a saw, and powdered. A reactor (internal capacity 10 ml) of SUS alloy was charged with 3.25 ml of distilled water, and 500 mg of the *Quercus crispula* material powder was added. Then, the inside of the reactor was purged fully with nitrogen, and the reactor was rapidly closed. The reactor was placed in a separately prepared resin bath (maintained in a mantle heater) kept at 380°C, and reaction was performed for 45 seconds. Then, the reactor was dipped in iced water for cooling. When the temperature of the contents reached 40°C, the reactor was opened. An aqueous solution was removed first, and then a tarry substance adhering to the wall was recovered with the use of ethyl alcohol. The resulting ethyl alcohol solution (about 10 ml) was treated with activated charcoal having a final concentration of 2,000 ppm. The composition of its constituents was examined by high performance liquid chromatography (carrier; Nakarai Tesk ODS reverse phase, mobile phase; 50-minute gradient elution with an aqueous solution containing 2% acetic acid to an aqueous solution containing 2% acetic acid and 25% methyl alcohol, flow rate 1 ml/min, detection wavelength 280 nm).

[0023] The results are shown in FIG. 1. The eluted aromatic compounds were used, unchanged, as a mixture, or used as an antioxidant after separation into compound groups or individual compounds by the same column chromatography. The aromatic compounds confirmed were gallic acid, protocatechuic acid, vanillic acid, syringic acid, vanillin, syringic aldehyde, coniferyl aldehyde, and sinapic aldehyde, in order of increasing retention time (shown by arrows in the drawing).

Example 2

[0024] A Japanese cedar material was cut thinly with a saw, and powdered. A reactor (internal capacity 10 ml) of SUS alloy was charged with 3.25 ml of distilled water, and 500 mg of the Japanese cedar material powder was added. Then, the inside of the reactor was purged fully with nitrogen, and the reactor was rapidly closed. The reactor was placed in a separately prepared resin bath (maintained in a mantle heater) kept at 380°C, and reaction was performed for 45 seconds. Then, the reactor was dipped in iced water for cooling. When the temperature reached 40°C, the reactor was opened. An aqueous solution was removed first, and then a tarry substance adhering to the wall was recovered with the use of ethyl alcohol. The resulting ethyl alcohol solution (about 10 ml) was treated with activated charcoal having a final concentration of 2,000 ppm. The composition of its constituents was examined by high performance liquid chromatography (carrier; Nakarai Tesk ODS reverse phase, mobile phase; 50-minute gradient elution with an aqueous solution containing 2% acetic acid to an aqueous solution containing 2% acetic

acid and 25% methyl alcohol, flow rate 1 ml/min, detection wavelength 280 nm).

[0025] The results are shown in FIG. 2. The eluted aromatic compounds were used, unchanged, as a mixture, or used as a perfume after separation into compound groups or individual compounds by the same column chromatography. The aromatic compounds confirmed were gallic acid, protocatechuic acid, vanillic acid, syringic acid, vanillin, syringic aldehyde, coniferyl aldehyde, and sinapic aldehyde, in order of increasing retention time (shown by arrows in the drawing).

Example 3

[0026] A hinoki material was cut thinly with a saw, and powdered. A reactor (internal capacity 10 ml) of SUS alloy was charged with 3.25 ml of distilled water, and 500 mg of the hinoki material powder was added. Then, the inside of the reactor was purged fully with nitrogen, and the reactor was rapidly closed. The reactor was placed in a separately prepared resin bath (maintained in a mantle heater) kept at 380°C, and reaction was performed for 45 seconds. Then, the reactor was dipped in iced water for cooling. When the temperature reached 40°C, the reactor was opened. An aqueous solution was removed first, and then a tarry substance adhering to the wall was recovered with the use of ethyl alcohol. The resulting ethyl alcohol solution (about 10 ml) was treated with activated charcoal having a final concentration of 2,000 ppm. The composition of its constituents was examined by high performance liquid chromatography (carrier; Nakarai Tesk ODS reverse phase, mobile phase; 50-minute gradient elution with an aqueous solution containing 2% acetic acid to an aqueous solution containing 2% acetic acid and 25% methyl alcohol, flow rate 1 ml/min, detection wavelength 280 nm).

[0027] The results are shown in FIG. 3. The eluted aromatic compounds were used, unchanged, as a mixture, or used as an antioxidant and a perfume after separation into compound groups or individual compounds by the same column chromatography. The aromatic compounds confirmed were gallic acid, protocatechuic acid, vanillic acid, syringic acid, vanillin, syringic aldehyde, coniferyl aldehyde, and sinapic aldehyde, in order of increasing retention time (shown by arrows in the drawing).

Example 4

[0028] A bamboo material was cut thinly with a saw, and powdered. A reactor (internal capacity 10 ml) of SUS alloy was charged with 3.25 ml of distilled water, and 500 mg of the bamboo material powder was added. Then, the inside of the reactor was purged fully with nitrogen, and the reactor was rapidly closed. The reactor was placed in a separately prepared resin bath (maintained in a mantle heater) kept at 380°C, and reaction was performed for 45 seconds. Then, the reac-

tor was dipped in iced water for cooling. When the temperature reached 40°C, the reactor was opened. An aqueous solution was removed first, and then a tarry substance adhering to the wall was recovered with the use of ethyl alcohol. The resulting ethyl alcohol solution (about 10 ml) was treated with activated charcoal having a final concentration of 2,000 ppm. The composition of its constituents was examined by high performance liquid chromatography (carrier; Nakarai Tesk ODS reverse phase, mobile phase; 50-minute gradient elution with an aqueous solution containing 2% acetic acid to an aqueous solution containing 2% acetic acid and 25% methyl alcohol, flow rate 1 ml/min, detection wavelength 280 nm).

[0029] The results are shown in FIG. 4. The eluted aromatic compounds were used, unchanged, as a mixture, or used as a perfume after separation into compound groups or individual compounds by the same column chromatography. The aromatic compounds confirmed were gallic acid, protocatechuic acid, vanillic acid, syringic acid, vanillin, syringic aldehyde, coniferyl aldehyde, and sinapic aldehyde, in order of increasing retention time (shown by arrows in the drawing).

EFFECTS OF THE INVENTION

[0030] The use of the process according to the present invention makes it possible to obtain useful aromatic compounds or their polymers in a shorter time and with more ease than conventional methods, and in the form of a mixture, compound groups, or individual compounds. Furthermore, by using, as plant materials, barrels after production of alcoholic drinks, materials hitherto handled as waste materials can be utilized effectively. The resulting aromatic compounds or their polymers can be put to a wide variety of uses, such as edible perfumes, flavors for luxury products, and aroma components for Japanese sake. When aromatic compounds are produced by the process of the present invention, moreover, waste as squeeze leavings discharged by conventional methods does not appear. Thus, the invention provides an environmentally-friendly technology.

Claims

1. A process for producing aromatic compounds or polymers thereof, comprising treating a plant material with supercritical water or subcritical water.
2. The process of claim 1, wherein the aromatic compounds are phenylpropanoids, a pyrogallol derivative, a pyrocatechol derivative, or a mixture of one or more of these compounds.
3. A process for producing plant-derived aromatic compounds or polymers thereof, comprising heating a plant material, together with water, in a pres-

surized container at a pressure of 100 to 300 atmospheres and a temperature of 250 to 500°C; then cooling the inside of the container to about 100°C or lower; extracting a tarry substance, which has been formed, with an organic solvent selected from the group consisting of alcohols, acetone, dimethyl sulfoxide, and acetonitrile; and isolating aromatic compounds or polymers thereof from the extract.

4. The process of claim 3, wherein the heating is performed at a temperature of 300 to 500°C and a pressure of 150 to 300 atmospheres to obtain aromatic compounds in a non-polymeric state.
5. The process of claim 3, wherein the heating is performed at a temperature of 250 to 400°C and a pressure of 100 to 250 atmospheres to obtain aromatic compounds as polymers.
6. The process of claim 3, wherein the heating at a pressure of 100 to 300 atmospheres and a temperature of 250 to 500°C is performed for 30 minutes or less, preferably 2 minutes or less, in an anaerobic state selected from a state under reduced pressure and a state in an inert gas.
7. The process of claim 6, wherein the plant material is a woody portion or a floral portion which has been chopped finely, cut thinly, or powdered.
8. The process of claim 7, wherein 1 part by volume of the plant material is heated together with 1 to 1,000, preferably 5 to 200, parts by volume of water in the pressurized container.

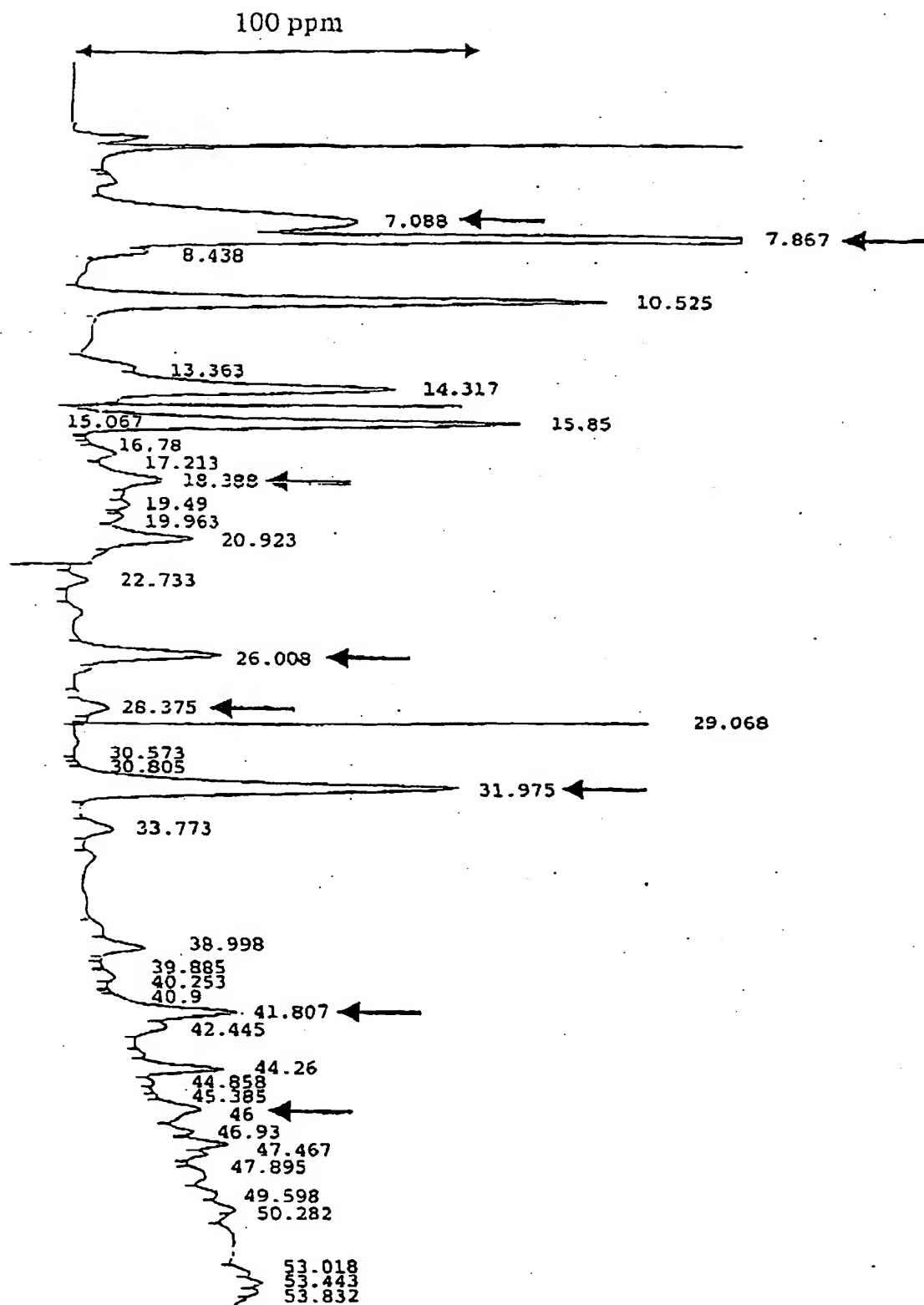


Fig. 1 AROMATIC COMPOUNDS FROM
QUERCUS CRISPULA MATERIAL

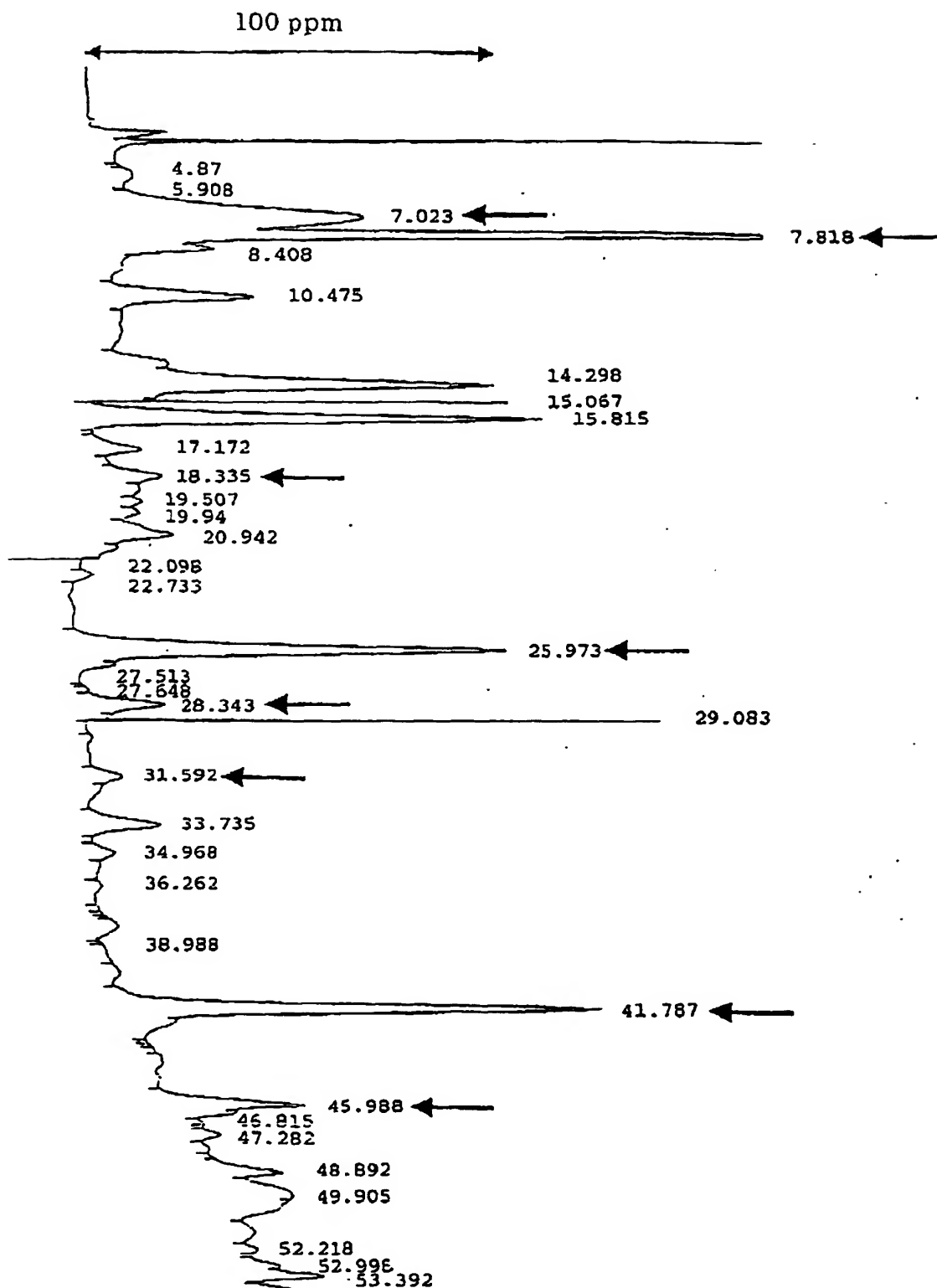


Fig. 2 AROMATIC COMPOUNDS FROM
JAPANESE CEDAR MATERIAL

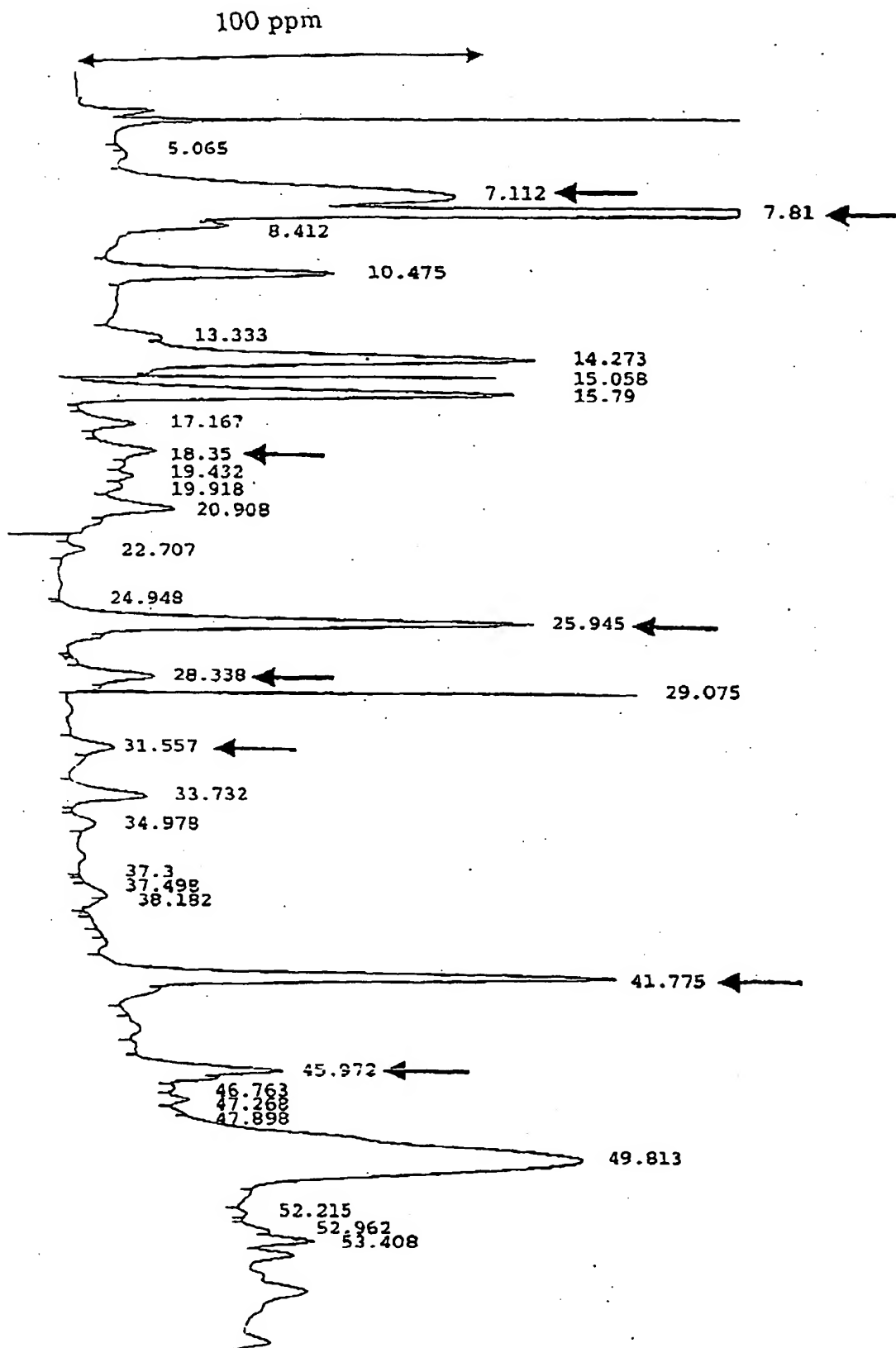


Fig. 3 AROMATIC COMPOUNDS FROM
HINOKI MATERIAL

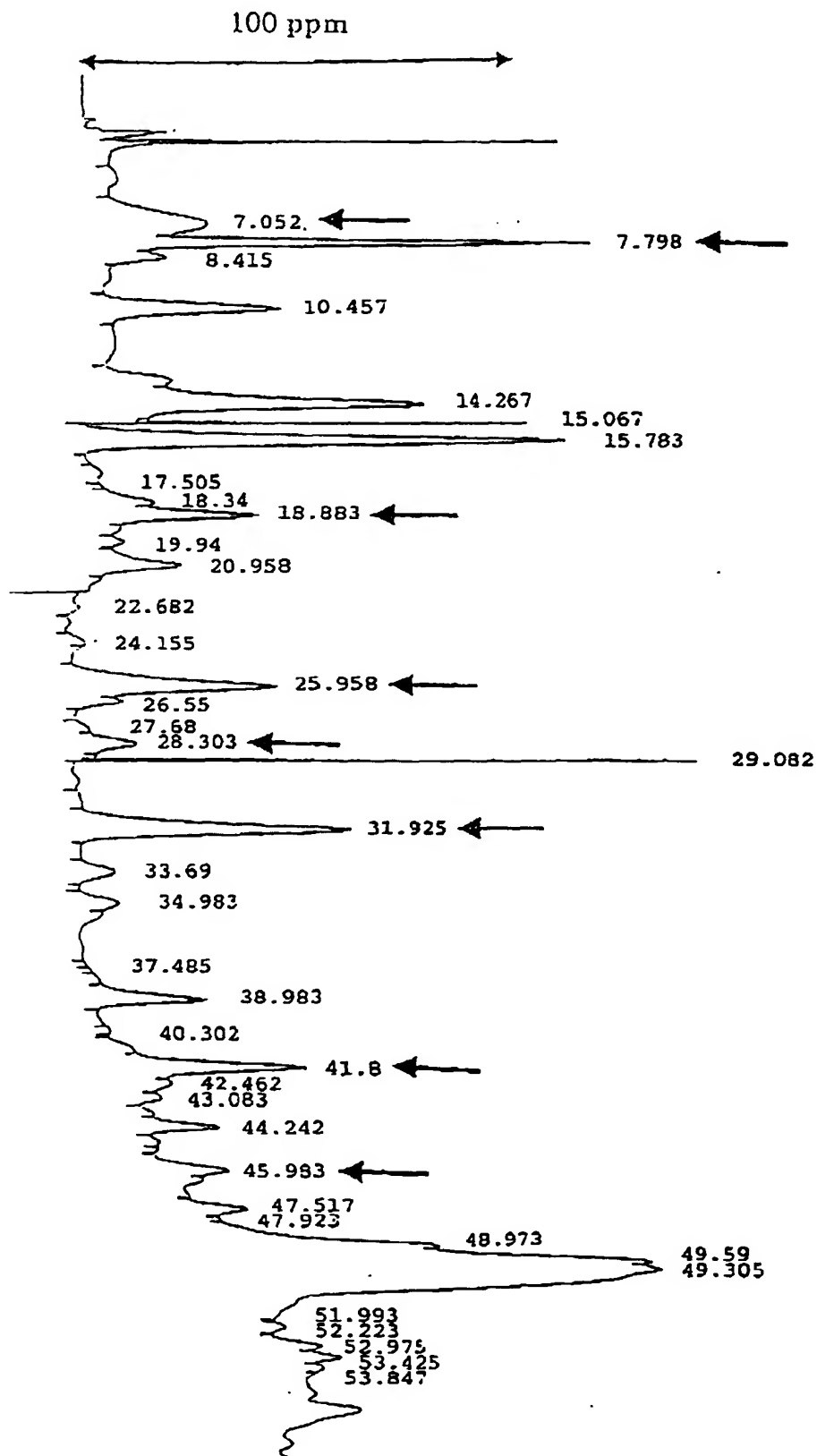


Fig. 4 AROMATIC COMPOUNDS FROM BAMBOO MATERIAL

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP99/01896

A. CLASSIFICATION OF SUBJECT MATTER
Int. Cl.⁶ C07B63/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl.⁶ C07B63/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CA (STN)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 56-501205, A (Modar Inc.), 27 August, 1981 (27. 08. 81) & WO, 81/855, A1 & GB, 2075050, A	1-8
A	JP, 1-203496, A (Fried Krupp GmbH.), 16 August, 1989 (16. 08. 89) & EP, 320813, A1 & DE, 3743058, A1 & US, 5011594, A	1-8
A	JP, 5-31000, A (Kobe Steel, Ltd.), 9 February, 1993 (09. 02. 93) (Family: none)	1-8
A	JP, 9-327678, A (Director General, Agency of Industrial Science and Technology), 22 December, 1997 (22. 12. 97) & DE, 19712045, A1 & US, 5777192, A & GB, 2314079, A	1-8
A	JP, 5-310602, A (Jumoku Chushutsu Seibun Riyon Gijutsu Kenkyu Kumiai), 22 November, 1993 (22. 11. 93) (Family: none)	1-8

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reasons (as specified)</p> <p>"Y" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p>
---	---

Date of the actual completion of the international search
17 June, 1999 (17. 06. 99)

Date of mailing of the international search report
29 June, 1999 (29. 06. 99)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

This Page Blank (uspto)